# MEASUREMENTS OF THE INITIAL STRAIN ENERGY OF LEATHER

by

CHENG-KUNG LIU AND MICHAEL D. MCCLINTICK

U. S. Department of Agriculture

Agricultural Research Service, Eastern Regional Research Center

600 East Mermaid Lane

Wyndmoor, PA 19038-8598

#### **ABSTRACT**

This investigation was to establish an improved method to characterize the stiffness of leather associated with its resistance to a small deformation while taking into account the nonlinear viscoelasticity of leather. Stiffness was quantitatively determined for a specimen by measuring the energy needed to stretch it to 10 percent strain. This physical quantity, called initial strain energy. was observed to be easier to define and measure than the tensile modulus. Using Box-Hunter's experimental design method a second order polynomial equation was derived for the relationship between initial strain energy and three major independent variables: moisture content, strain rate, and sampling angle. The breaking elongation was observed to decrease as initial strain energy increased, whereas the tensile strength did not show a direct correlation with initial strain energy alone. However, regression analysis provided a significant statistical relationship between tensile strength and a parameter that incorporates the effects of strain energy, moisture content and strain rate. Thus, a prediction of tensile strength may become feasible based on measurements of initial strain energy without breaking the leather.

#### Introduction

Tensile modulus is one of the most important physical quantities characterizing the mechanical properties of leather. It expresses the resistance of leather subjected to a small tensile deformation. It is commonly known that the higher the tensile modulus, the stiffer the leather is. Theoretically, it has been linked to the fine structure of leather such as the degree of fiber orientation<sup>1,2</sup> and fiber adhesion.3 In practical terms, this physical quantity has been associated with leather softness, temper, and handle.4.5 In fact, its reciprocal has been named compliance in the literature.6 Adequate softness or pliability is a very important quality requirement for certain leather products particularly for garments, upholstery and footwear. It provides comfort and good handling to the user. The quantitative assessment of softness or its reverse term "stiffness" can be based on measurements of the resistance to a small deformation by tensile, shear, compression or bending forces. The resistance may be best quantitatively represented by the initial slope of the load-displacement curves or the stress-strain curves in the elastic deformation region, i.e. the tensile modulus (elastic modulus) and shear modulus. The shear modulus is more difficult to measure than the tensile modulus; however, if a material's Poisson's ratio is relatively constant, as it is for leather,7 then the shear modulus is approximately proportional to the tensile modulus.8.9 Therefore, the tensile modulus has been one of the most important physical characteristics studied and discussed by leather scientists. It has been known to be extremely sensitive not only to changes of composition, moisture, and fatliquor concentration, but also to various leathermaking processes such as drying and staking.

The measurement of tensile properties is known to be a routine quality control test in the leather industry, including tensile strength and breaking elongation as described in ASTM D2209-95<sup>10</sup> and ASTM D2211-95.<sup>11</sup> However, the tensile modulus normally is not included in the test list. Instead, the softness test is performed separately by various empirical methods such as the torsion wire stiffness test as

described in ASTM D2821-79, and those reported by Alexander and Stosic, 13 including the Peirce flexometer test, 12 the vertical loop test, and the cylinder compression test. Probably the reason is that tensile modulus is difficult to define for leather materials because leather is not perfectly elastic even for a small deformation. The closest approximation of this modulus can be obtained from the slope of a tangent line made through the initial deformation region of the load-displacement or stress-strain curves. The procedure can be very time consuming and data so obtained often is difficult to reproduce. Therefore, several alternative methods have been used to estimate tensile modulus, such as measurement of the secant modulus. For example, Maeser<sup>14</sup> measured the slope of the line joining the origin and a selected point at 10 percent strain; and Attenburrow and Wright<sup>15</sup> measured the slope of the line joining the 1 percent and 2 percent strain. Strictly speaking, these alternative methods do not provide complete information of the resistance of initial tensile deformation because they do not take the non-linear nature of initial stress-strain behavior into account.

In order to more effectively optimize leather making processes, the proper characterization of its physical quantities is essential. Our ongoing research projects on improving the processing and properties of leather has propelled us to look for a parameter which can quantify the . initial deformation resistance of leather. This physical quantity should not be ambiguous to define and should be easy to measure. Consequently, an effort has been made to develop a methodology for characterizing the resistance of leather to a small deformation. We have exploited a new method for measuring the resistance of initial deformation. Instead of measuring the slope of secant lines or tangent lines we measured the energy needed to stretch leather to determine the resistance of deformation. By integrating the area under the initial load-displacement curves from the origin up to 10 percent strain, we have quantitatively characterized the initial resistance to deformation of leather samples. This calculation can be readily performed by using microcomputers and appropriate software.

Most of the discussion in the past on the physical characterization of leather has been in a qualitative manner. In order to present the experimental results in a quantitative way for this study, we have used the technique of experimental design along with factorial analysis to treat data and to obtain mathematical models. Because of the lengthy calculations involved, the application of those statistical methods seemed to be a cumbersome technique in the past, but the present widespread use of microcomputer technology and statistical software such as the SAS software

system has made the task easier, and it is now possible to make calculations in a reliable and rapid manner. We systematically studied three major independent variables affecting initial strain energy: strain rate, moisture content, and sampling angle. Because of their importance to leather quality, the effects of fatliquoring and staking on the initial strain energy were also included in the study. Finally, we also formulated statistical relationships between the initial strain energy and tensile strength, as well as breaking elongation. The rationale for these relationships associated with the fibrous nature of leather and test conditions is elucidated.

### EXPERIMENTAL

#### **M**ATERIALS

Previously frozen, mature bovine hides were tanned by the standard ERRC process<sup>17</sup> and were air-dried without fatliquors. The samples were then split to a thickness of 2 mm and were stored in a conditioned room at 23°C and 50 percent RH. These samples, without fatliquoring and staking, were used in an experimental design as described in the next section. To study the effects of fatliquoring and staking two sides of frozen mature bovine hides were chrome-tanned by the same process described before. Each side was then divided evenly between the tail and neck ends. The tail end half of each side was treated to 5 percent with Reilly-Whiteman (Conshohocken, PA) fatliquor X-76-31, a "solvent-type oil," 2 percent sulfated. 18 The neck end half of each side was left untreated. Then, one of the sides was dried at constant area at room temperature in still air and passed through a Molissa staking machine. The other side was dried similarly but without staking, and provided control samples for comparison. Rectangular samples 10 x 100 mm were cut for tensile testing from the standard test areas as described in ASTM D2813-91. The moisture content was determined for samples having less than 20 percent moisture right before tensile testing by a Delmhorst moisture meter (Delmhorst Instrument Co.); higher moisture levels were measured by the gravimetric method. A typical cross-sectional view of samples is demonstrated in Figure 1. It comprises about 0.6 mm of grain layer and 1.4 mm of corium layer with numerous fiber bundles interwoven together.

#### STATISTICAL DESIGN OF EXPERIMENTS

Box and Hunter's "response surface methodology" technique of experimental design was applied to the design of the study and to analysis the data.<sup>19</sup> The three factors selected were the strain rate  $(x_1)$ , moisture content  $(x_2)$ , and sampling angle  $(x_3)$ . Originally, there were 23 combinations of factors required by this particular design. However, we

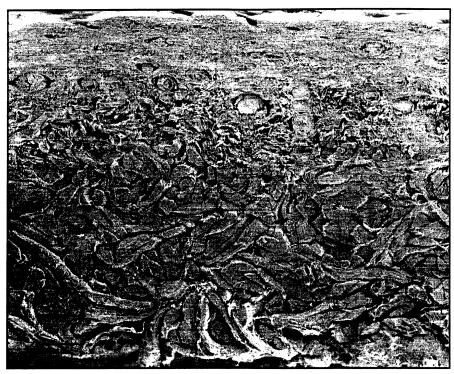


FIGURE 1. — The cross-sectional view of a leather sample.

later found that widening the range of variables for moisture content was necessary to obtain a more comprehensive model. Therefore, an additional 16 combinations of factors were added to the design. Table I is the matrix showing the combinations of coded levels for the three factors for each of the thirty nine experimental conditions. A regression model was derived having the form of a polynomial equation in which the variables are presented as their linear and quadratic terms as well as their bifactorial cross products:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{11} x_1^2 + b_{22} x_2^2 + b_{33} x_3^2 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3$$
 (1)

In this equation Y is the response: initial strain energy; and  $b_i$ ,  $b_{ij}$  are the corresponding regression coefficients of the polynomial equation. These coefficients along with analysis of variance can be obtained readily by using SAS software version 6.11 with a microcomputer. The levels of the coded variables  $x_1$ ,  $x_2$ ,  $x_3$ , were obtained by means of the following formulae, where  $x_1$ ' (mm/min),  $x_2$ ' (percent),  $x_3$ ' (degree°), are the variables with original scales:

$$x_1 = (x_1'-200)/100$$
  
 $x_2 = (x_2'-15)/3$  (2)  
 $x_3 = (x_3'-0)/45$ 

The sampling angle is designated as  $0^{\circ}$  for the direction perpendicular to the backbone line and as  $90^{\circ}$  for the direction parallel to the backbone.

## MEASUREMENT OF THE INITIAL STRAIN ENERGY

The initial strain energy of leather is defined as the energy needed to stretch the leather to 10 percent strain. If we consider a sample under a load F increasing in length by an amount dl, the energy needed to stretch the leather to 10 percent strain is given by the following expression:

$$\int_{Q}^{10\%} Fdl \tag{3}$$

This is the area under the load-displacement curve from 0 to 10 percent strain (Figure 2). The load-displacement curve can be readily converted to the so called "stress-strain curve" by simply dividing load by cross-section area of test sample for the former and dividing displacement by the original length of test sample for the latter. If the thickness and length of samples are relatively constant, as in this study, then these curves essentially have the same pattern. We use the term load-displacement curve because it is easier to relate to the energy data which is F•dl.

If other material variables are equal, the initial strain energy of leather will be proportional to the mass of tested samples. To compare different samples, the value of expression 3 for each test sample was divided by the mass of that sample to obtain the initial strain energy with the SI units of J/g.

TABLE I Experimental Plan

	가 되는 것이 되어 있습니다. 그리는 이 맛이 얼굴하게 되었다.	<b>Coded Values</b>	
Run	$\mathbf{X_{1}}$	$X_2$	$X_3$
1	1	1	-1
2	1	-1	-1
3	0	1.68	0
4	0	0	0
5			1
6	0	0	0
7	0	0	0
8	0	-1.68	0
9	1		-1
10	1.68	0	0
11	0	0	0
12	0	0	1.68
13	0	0	0
14	0	0	0
15	0	0	-1.68
16	-1	<b>-1</b>	1
17	, N	01,040,000	0
18	0		0
19	0	<b>0</b>	0
20	-1.5		0
21			1
22	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		-1
23			1
24	0	-0.67	2
25	0	18.33	-2
26	0	23.67	2
27	0	22.67	2 -2 2 -2 -2 2
28	0	27	2
29		30.33	-2
30	0	-0.67	-2
31		1.67	2
32	0	4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	-2
33	0	2	
34		10	2 -2
35	0	12.67	0
36	0	-5	0
37	0	-5	0
38	0	-5 - 1 - 5 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -	2
39		-5	2 -2
			·

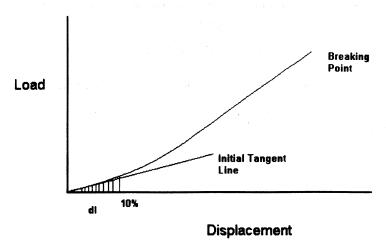


FIGURE 2. — Initial strain energy.

An Instron tensile testing machine was used throughout this work. The initial strain energy was measured as shown in Figure 2. For comparison, Young's modulus was estimated by measuring the slope of a tangent line for the stress-strain curves from the origin to 10 percent strain. All of the data were calculated and collected through Instron series IX automated materials testing sofware version V. The tensile strength of leather was measured at 23°C and 50 percent RH with a gauge length of 50 mm. The strain rate was adjusted according to the experimental design listed in Table I.

### RESULTS AND DISCUSSION

STATISTICAL MODEL AND ANALYSIS OF VARIANCE .

Table II shows the matrix of test results corresponding to the experimental design matrix listed on Table I. The data was processed by the SAS statistical program based on Box and Hunter's design using a microcomputer. Table III shows the regression coefficients of the statistical model, corresponding t values, and significant levels for each coefficient. A second order regression model can be expressed as follows:

$$Y = 24.8 - 1.98x_1 - 1.67x_2 - 3.06x_3 + 1.17x_1^2 + 0.024x_2^2 + 3.98x_3^2 + 0.082x_1x_2 + 1.96x_1x_3 + 0.093x_2x_3$$
(4)

As indicated in Table IV for the analysis of variance, both the linear and quadratic terms give significant mean square values. The correlation coefficient (R) for this quadratic model is 0.82. Moreover, Table IV also indicates that the cross-product term may be neglected because of a high probability of coming from experimental error. A simplified second-order model thus may be expressed as:

Y (J/g x 
$$10^{-2}$$
) = 24.8 - 1.67 x<sub>2</sub> - 3.06 x<sub>3</sub> + 0.024 x<sub>2</sub><sup>2</sup> + 3.98 x<sub>3</sub><sup>2</sup> (5)

STRAIN RATE

It is well known that the rate of stretching (strain rate) has profound effects on the results of mechanical properties testing. However, the current test procedure described in ASTM only uses one strain rate (cross-head speed), which is 254 mm/min. There have been some reports describing the effects of strain rate on the breaking load and elongation of collagen fibers, but not for leather as a whole. Morgan reported that when samples of untanned collagen fibers taken from cow hide were tested at 0, 33, and 66 percent relative humidity (RH), tensile strength and elongation initially increase with rate of loading, then decrease. The results were rather different when tested at 100 percent RH. the tensile strength and elongation increased monotonously with strain rate. A more recent study by Arumugam et al. showed that the tensile strength increased with increasing strain rate when tested at 65 percent RH for both tanned and untanned collagen fibers taken from the tails of male albino rats. It was also demonstrated that the slope of the stressstrain curves increased with increasing strain rate for both chrome tanned and formaldehyde tanned collagen fibers. We have found in an earlier investigation that strain rate is a complex factor when acting upon fibrous materials such as leather. The energy needed to fracture a leather sample first decreased then increased with increasing strain rate. The increasing heat generated during high speed stretching induced an effect of plasticization upon the fiber bundle and therefore increased the fracture resistance of the leather.

Figure 3 is a 3-D plot of the response surface according to Equation 4 for the 0° sampling angle. Figure 4 is a plot of the contour curves of initial strain energy data. They

TABLE II
Experimental Results

37.7	51.6
	31.0
45.3	60.9
12.4	14.6
15.8	21.6
19.6	38.5
32.1	40.6
17.2	20.8
29.6	50.4
28.5	31.6
23.4	30.2
	28.7
	44.9
	41.2
	23.3
	60.2
	35.7
	34.7
	24.7
	36.7
	28.6
	23.3
	68.2
	31.7
	46.9
	26.1
	22.4
	22.7
	16.2
	22.2
	45.4
	40.4
	40.4
	55.3
	43.6
	20.7
	57.6
	57.0 57.3
	53.5 64.0
	15.8 19.6 32.1 17.2 29.6 28.5

TABLE III
Regression Coefficients

Parameter	Degrees of Freedom	Regression Coefficient	Standard Error	t for $H_0$ : Regression Coefficient = 0	Probability >   t
Intercept	<b>1</b> 1000	24.762	2.03	12.21	0.00
X <sub>1</sub>	1	-1.982	2.16	-0.09	0.37
$X_1$ $X_2$	1	-1.667	0.44	-3.81	0.00
$X_2$ $X_3$	1	-3.056	1.16	-2.63	0.01
$X_{1}^{2}$	. 1	1.173	2.02	0.58	0.57
$X_1 * X_2$	1	0.082	2.75	0.03	0.98
$X_1$ $X_2$ $X_2^2$	1	0.024	0.02	1.33	0.19
$X_1 * X_3$	1 .	1.961	2.75	0.71	0.48
$X_1 \times X_3 \times X_2 \times X_3$	1	0.093	0.08	1.12	0.27
$X_2$ $X_3$ $X_3^2$	1	3.985	0.84	4.77	0.00

 $<sup>*</sup>H_0$  = null hypothesis

TABLE IV

Analysis of Variance for Second-Order Model

Regression	Degrees of Freedom	Sum of Squares	F-Ratio	Probability > F
Linear	3	1928.861	10.656	0.0001
Quadratic	3	1530.170	8.453	0.0003
Cross product	3	106.724	0.590	0.6268
Total Regress	9	3565.755	6.566	0.0000

\*F-Ratio = variance ratio

clearly show that the strain rate has very little effect on the initial strain energy. The statistical analysis as mentioned earlier has indicated that the strain rate is not a significant factor in determining the initial strain energy. Evidently, when leather samples were subjected to a small stretch, such as 10 percent strain, the rate of stretching did not affect the amount of energy needed to cause the deformation. This behavior is very different from that of collagen fibers or any other fibers. Meredith<sup>22</sup> found that the tensile modulus increased almost linearly with log(strain rate) for various fibers including rayon, acetate, silk and nylon. Hall<sup>23</sup> also reported a similar behavior for polyester and acrylic fibers.

This behavior can be attributed to the viscoelasticity of the fibers, in that besides the elasticity, the viscous component or viscosity plays an important role in determining the stress-strain curve even at the very beginning of deformation. When fibers are stretched under a constant strain rate, the stress response will be a function of time, and stress-strain tests take some time, and consequently there is an opportunity for stress relaxation to occur. The faster the test, the less time there is available for stress relaxation to occur, thus the greater the stress at a given strain, consequently the stress per unit strain is higher, and in other words, the tensile modulus is higher.

t = Student's t = (regression coefficient/standard error)

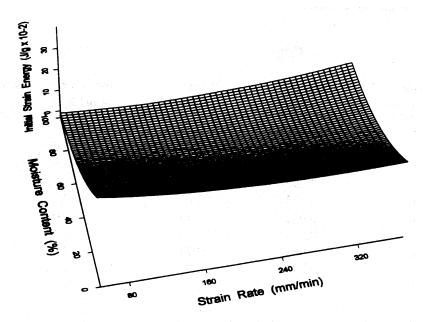


FIGURE 3. — Effect of strain rate for sampling angle at 0° shown by 3-D plot.

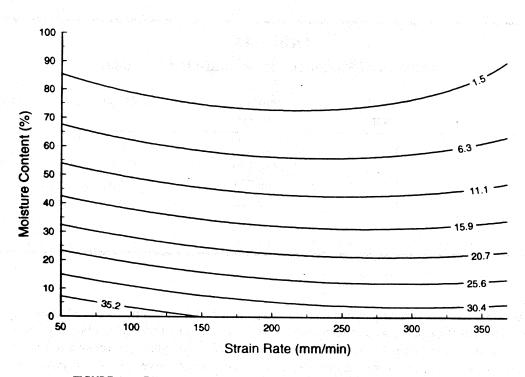


FIGURE 4. — Effect of strain rate for sampling angle at 0° shown by contour plot

Viscoelasticity explains fairly well the effect of strain rate on homogenous materials such as fibers or polymeric solids or fluids. Leather, however, has a very complex structure, consisting of a network of interwoven fiber bundles with large spaces unevenly distributed among them. Fiber bundles (20-200 µm) are comprised of very fine element fibers (10 µm), which can further be divided into even finer fibrils (0.01-0.5 µm).24 In the early deformation phase, only fiber bundles start to stretch or bend to decrimp because they have more spaces to move around and expend less energy. In contrast, fibrils or element fibers probably have very little deformation because they are strongly bonded by minority collagens and twisted together. We believe the resistance to early small deformation comes largely from friction and some degree of adhesion between fiber bundles. Resistance force due to fiber adhesion is generally governed by linear viscoelasticity, which has provided an explanation for the strain rate effects on the collagen fibers. However, the resistance due to friction of the fiber bundles in leather may not be explained simply by viscoelasticity. Friction coefficients have been reported to vary with speed of motion.<sup>25,26</sup> It is very possible that as strain rate increases. the friction coefficient decreases, thereby lowering the friction force, and thus balancing out the increasing stress due to the viscoelasticity effect. Consequently, the initial strain energy is not affected by change of strain rate.

#### MOISTURE CONTENT

Figures 5 (3-D plot) and 6 (contour curve plot) clearly show that the initial strain energy decreases with increasing moisture content of leather. The behavior of water functioning as a lubricant is well known. Water eases the movement of fibers and decreases the frictional resistance between fibers when leather is subjected to a force. On the other hand, Kronick<sup>27</sup> has linked the effects of moisture content to the fiber adhesion in leather. He demonstrated that as moisture content increased in leather subjected to a tensile stress the acoustic emission decreased. This effect occurs because water disrupts the fiber adhesion, thereby reducing the sound emitted during the tensile test. Consequently, this provides additional reasoning for lowering the initial strain energy by increasing moisture content.

#### SAMPLING ANGLE

Figures 7 and 8 illustrate the initial strain energy as a function of sampling angle and strain rate. The sampling angle shows a significant effect on initial strain energy. Leather has been known as a highly anisotropic material. In a very comprehensive study, Maeser<sup>14</sup> demonstrated that the tensile modulus estimated by the secant slope method to 10 percent strain was highly sensitive to the sampling angle.

This is not surprising because the tensile modulus has been known to be strongly associated to the fiber orientation in leather. Tensile modulus measures stress in the one direction that the sample is being stretched. The more fiber bundles that line up in the test direction, the higher the tensile modulus value that obtained. In fact, our tests have shown the initial strain energy is greater at close to the parallel direction than at any other sampling angle, as illustrated in Figure 7.

# COMPARISON BETWEEN INITIAL STRAIN ENERGY AND YOUNG'S MODULUS

The parallel relationship between initial strain energy and Young's modulus is illustrated in Figure 9. It shows an excellent linear correlation (R=0.95) between these two physical quantities. A theoretical line was constructed in Figure 9 based on Equation 6; this is a straight line that obeys the Hooke's law of elasticity. If leather samples follow perfect elastic behavior, i.e., Hooke's law, the strain energy can simply be expressed by the following equation:

$$Y(J/g) = \frac{1}{2} \cdot M_o \cdot A \cdot (\varepsilon)^2 L_o / W_o \tag{6}$$

In this equation Y is initial strain energy,  $M_o$  is Young's modulus,  $\epsilon$  is strain,  $L_o$  is the sample test length. A is the area of cross section, and  $W_o$  is the weight of the test sample.

The deviation of initial strain energy from the linear relationship simply indicates the stress-strain curve up to 10 percent strain does not fully obey Hooke's law. Nevertheless, Figure 9 demonstrates a correlation between these two physical parameters. Although the methods used to determine these two physical quantities are different, both may serve the same function to characterize the resistance to initial deformation of leather. However, the initial strain energy method takes the non-linear viscoelasticity of leather into account and is easier to measure and to define as mentioned earlier.

Besides 10 percent initial strain energy, we also measured 5 percent initial strain energy; the latter parameter showed much more variability. This may be attributed to the experimental error incurred from the crimp of the leather sample if it was not fully straightened out by the initial load applied to the samples.

#### EFFECTS OF FATLIOUORING AND STAKING

Fatliquoring is a process of adding oil, which lubricates the leather fibers so that after drying they will more easily slip over one another. This process has been practiced in leather

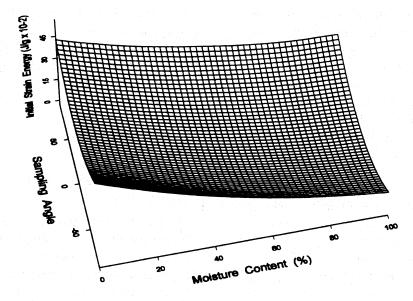


FIGURE 5. — Effect of moisture content on initial strain energy shown by 3-D plot.

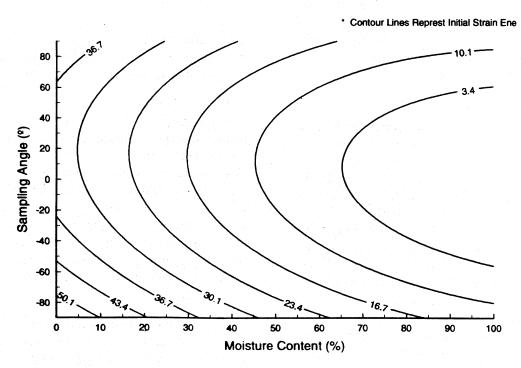


FIGURE 6. — Effect of moisture content on initial strain energy shown by contour plot.

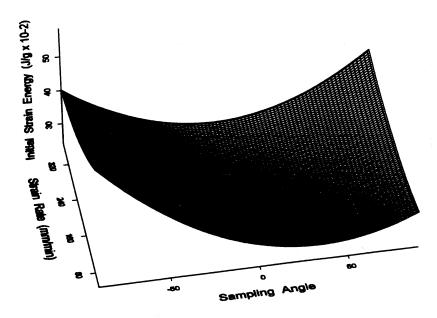


FIGURE 7. — Effect of sampling angle on initial strain energy shown by 3-D plot.

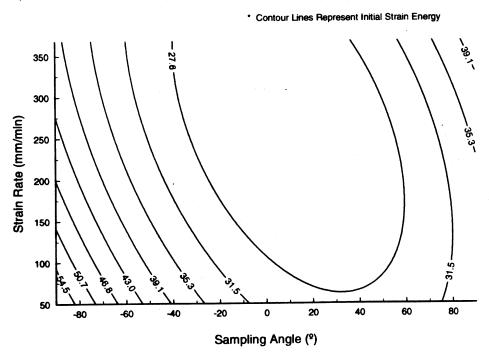


FIGURE 8. — Effect of sampling angle on initial strain energy shown by contour plot.

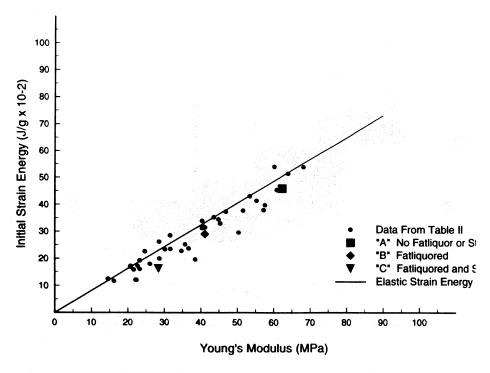


FIGURE 9. — Correlation between initial strain energy and Young's modulus.

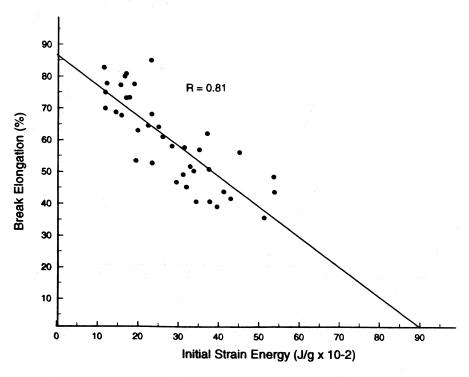


FIGURE 10. — Correlation between initial strain energy and breaking elongation.

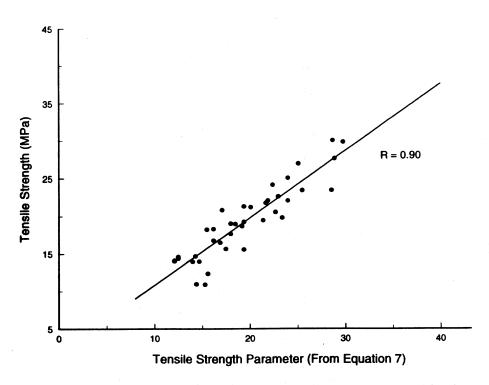


FIGURE 11. — Statistical modeling to predict tensile strength based on measurements of initial strain energy.

making to improve the flexibility and softness of leather. The effect of fatliquoring on leather properties can be seen in Figure 9, where A is the control sample, and B has been fatliquored as described in the Experimental section. Both Young's modulus and initial strain energy of the fatliquored samples are much smaller than those of the control samples.

The staking process subjects leather to a very large number of rapid oscillating, stretching and flexing operations. it is an additional process in leather making used to enhance the pliability of leather. In combination with the correct fatliquoring treatment, staking governs the final firmness or softness of the leather. This mechanical action is necessary to break weak adhesions within the fiber structure, thereby promoting the mobility of the fibers.<sup>27</sup> The mechanical stresses that staking impose on the leather are very great, and if overdone staking can adversely affect leather integrity.<sup>28</sup> As shown in Figure 9, sample C has been subjected to staking in addition to fatliquoring; this yields Young's modulus and initial strain energy values significantly lower than those for the fatliquored-only samples B.

# CORRELATION BETWEEN INITIAL STRAIN ENERGY AND TENSILE STRENGTH AND BREAKING ELONGATION

An attempt was made to correlate the initial strain energy to the other two important tensile properties: tensile strength and breaking elongation. As illustrated in Figure 10, the breaking elongation decreases with increasing initial strain energy. This implies that factors promoting the fiber mobility in leather not only reduce the resistance to small deformation but also go further to increase the ultimate strain (breaking elongation). Those factors can be moisture, fatliquor, staking, and a lower degree of fiber orientation in leather as described previously. Initial strain energy faithfully reflects the nature of leather structure factors such as fiber orientation (associated with sampling angles) and fiber adhesion. Higher initial strain energy reflects a more ordered structure in the leather with a higher degree of fiber orientation in the direction of the applied strain, which offers higher resistance to a small deformation; the result is stiffer leather. The same structural factors that cause higher initial strain energy also do not favor fiber movements; therefore samples with high initial strain energy have less breaking elongation. The relationship between initial strain energy and tensile strength, however, is not straightforward; in fact there was no direct correlation found in a statistical analysis. The main reason is that the factors of moisture content and strain rate do not give parallel effects on these two physical quantities. For example, moisture, acting as a lubricant, reduces frictional resistance and also lessens fiber adhesion, therefore decreasing initial strain energy. However, moisture affects not only the initial deformation, but also makes the fibers move more easily to an orientation parallel to the applied force direction; this increases the load bearing ability and enhances the resistance to fracture of the leather sample, which consequently increases the tensile strength.

An effort was made to establish a parameter that incorporates together the initial strain energy and the test conditions, and then to relate this parameter to tensile strength by combining two regression equations (one for initial strain energy and the other for tensile strength). After statistically non-significant factors are removed, a polynomial equation modeling this relationship can be expressed as follows:

$$TS = Y + 7.33 - 2.35x_1^2 - 1.04x_2 - 0.02x_2^2$$
 (7)

In this equation TS is tensile strength in MPa, and Y is initial strain energy in 10-2 J/g. Statistical analysis shows that Equation 7 has a correlation coefficient of 0.90; therefore this statistical model is justifiable. Figure 11 demonstrates a fair agreement between the experimental data (shown as open circles) and predicted data (shown as a straight line) based on Equation 7.

Although Equation 7 is a statistical model based on regression analysis, its implications are rather reasonable. It is interesting to note that sampling angle (x<sub>3</sub>) is not shown in the model because it has been incorporated into initial strain energy. Therefore, the effect of sampling angle on TS value will be embedded in the effect of initial strain energy. In other words, measuring the effect of the sampling angle on initial strain energy is equivalent to measuring its effect on tensile strength. Consequently, if we measure the initial strain energy at any sampling angle and know the strain rate and moisture content we will be able to predict ultimate tensile strength, based on Equation 7, without the need to break the leather. This could be very valuable in semi-product quality control. If a small tensile tester can be designed to stretch leather 10 percent and measure initial strain energy, then knowing the strain rate and moisture content would enable one to estimate the final tensile strength without breaking the leather. Of course, the statistical model must first be established for different types of leather and different beamhouse conditions.

# Conclusions

Our essential objective for this investigation was to establish an improved method to characterize the resistance of leather to a small deformation while taking into account the nonlinear viscoelasticity of leather. By measuring the strain energy up to 10 percent strain, we are able to readily characterize the resistance of a leather sample to deformation by using a tensile tester and a microcomputer. The traditional method of determining the tensile modulus is

based on measuring the slope of the initial portion of the stress-strain curve, which is not only time consuming but also does not agree with the complex structure of leather, which is a nonlinear viscoelastic material even at small deformation.

We have utilized the techniques of experimental design and statistical analysis to mathemetically model the influence of strain rate, moisture content and sampling angle upon the initial strain energy. Results show that strain rate has no significant effect on the initial strain energy. This is because the effect of strain rate on the friction coefficient balances out the effect of strain rate on stress relaxation. Water acts as a plasticizer, lubricating the fiber bundles and decreasing friction resistance and fiber adhesion, therefore reducing the initial strain energy. Moreover, similar to its effect upon tensile strength and breaking elongation, the sampling angle was shown to have a pronounced effect on the initial strain energy. The leather samples taken from closer to the parallel direction have higher strain energy than those of the perpendicular direction. This again demonstrates the strong anisotropic nature of the fibrous structure of leather. Staked and fatliquored leather clearly showed a reduced initial strain energy. This is due to the staking operation's breaking the fiber adhesion and fatliquors' adding lubricity to the leather fibers. In this paper we have also demonstrated a correlation between initial strain energy and Young's modulus. This is not surprising, because in nature both are measuring the resistance to initial deformation, though the latter is measuring the initial slope of stress-strain curves that is often not easy to define and is time consuming. We also demonstrated that a correlation existed between initial strain energy and breaking elongation. On the other hand initial strain energy does not show any direct correlation to tensile strength.

A statistical model was established for the relationships among tensile strength, initial strain energy, strain rate, and moisture content. This finding may have a significant application in nondestructive evaluation of tensile strength for partially processed leather before fatliquoring and staking. For those early stage semi-products, we may simply stretch the leather to 10 percent, measuring the initial strain energy at any sampling angle, and be able to predict the tensile strength without breaking the leather.

### ACKNOWLEDGMENTS

We wish to thank Dr. John G. Phillips for advice on statistical experimental design and the use of SAS software. We also thank Dr. Paul Kronick for his advice. Particular

appreciation is extended to Mr. Randall L. Rowles, Chairman of the Committee on Methods, ALCA at Leather Industries Research Laboratory, University of Cincinnati for his invaluable suggestions.

# REFERENCES

- 1. Kronick, P. L., and Buechler, P. R.; "Fiber Orientation in Calfskin by Laser Light Scattering or X-ray Diffraction and Quantitative Relation to Mechanical Properties," *JALCA* 81, 221-230, 1986.
- 2. Kronick, P. L., and Buechler, P. R.; "Fiber Orientation and Small-Deformation Modulus of Stretched, Partially Dried Hide," *JALCA* 83 (4), 115-124, 1988.
- 3. Kronick, P. L., Page, A., and Komanowsky, M.; "An Acoustic Emission Study of Staking and Fatliquor," *JALCA* 88 (5), 178-186, 1993.
- 4. Guy, R.; "A Comparison of Some Foot Comfort Properties of a Full Chrome Side Leather and 'Porvair'," BLMRA J. 15 (3), 65-68, 1972.
- Diebschlag, W.; "Measurements of the Elasticity of Different Shoe-Upper Materials As Well As Their Maximum Pressure on the Foot During Walking," Leder 26 (1), 7-18, 1975.
- 6. Morton, W. E., and Hearle, J. W. S.; "Physical Properties of Textile Fibers," The Textile Institute, Manchester and London, 272, 1978.
- 7. Kinnersley, G. A., and Marriott, "A Fundamental Study of Some Non-Ultimate Physical Properties of the Leather, Part I. Leather in Extension," Lr-91, 36, 1979.
- 8. Van Vlack, L. H.; "Elements of Materials Science and Engineering," 4 ed., Addison-Welsey, Reading, Massachusetts, 193, 1980.
- 9. Stippes, M., Wempner, G., Stern, M., and Beckett, R., "The Mechanics of Deformable Bodies," Charles E. Merrill, Columbus, Ohio, 183, 1961.
- 10. American Society for Testing Materials, Annual Book of ASTM, Vol 15.04, D2209-95 and D2211-95, 1995.
- 11. American Society for Testing Materials, Annual Book of ASTM, Vol. 15.04, D2211-95, 1995.
- 12. Peirce, J. Text. Inst., 21 T377, 1930.

- 13. Alexander, K. T. W., and Stosic, R. G.; "A New Non-Destructive Leather Softness Test," *JSLTC* 77 (5), 139-142, 1993.
- Maeser, M.; "The Effect of Hide Location and Cutting Direction on the Tensile Properties of Upper Leathers," JALCA 55, 501-530, 1960
- Attenburrow, G. W., and Wright, D. M., "Studies of the Mechanical Behavior of Partially Processed Leather," *JALCA* 89, 391-402, 1994.
- 16. Cochran, W. G. and Cox, G. M.; "Experimental Designs," John Wiley & Sons, New York, 335, 1951.
- 17. Taylor, M. M., Diefendorf, E. J., Hannigan, M. V., Artymyshyn, B., Pillips, J. C., Feairheller, S. H., and Bailey, D. G.; *JALCA* 81, 43-61, 1986.
- Kronick, P. L., Page, A., and Komanowsky, M.; "An Acoustic Emission Study of Staking and Fatliquor," *JALCA* 88, 178-186, 1995.
- 19. Box, G. E. P., and Hunter, J. S., "Multifactor Experimental Designs," Ann. Math. Stat., 28, 1957.
- 20. Morgan F. R., The Mechanical Properties of Collagen and Leather Fibers," J. Soc. Leath. Tech. Chem. 55, 4-23, 1960.
- 21. Arumugam, V., Naresh, M. D., Somanathan, N., and Sanjeevi, R.; "Effect of Strain Rate on Crosslinked Collagen Fibers," *J. Soc. Leather Tech. Chem.* **79** (5). 143-147, 1995.
- 22. Meredith, R.; J. Text. Inst. 45, T30, 1954.
- 23. Hall, I. H.; J. Appl. Polymer Sci. 12, 731-739, 1968.
- 24. O'Flaherty, F., Roddy, W. T., and Lollar, R. M.; "Chemistry and Technology of Leather," Vol. 1, 115. 1956.
- 25. Morton, W. E., and Hearle, J. W. S.; "Physical Properties of Textile Fibers," The Textile Institute, Manchester and London, 621, 1978.
- 26. Roder, H. L., J. Text Inst. 46, 84, 1955.
- 27. Kronick, P. L. and Page, A.; "Recovery of Properties of Staked Leather on Storage," *JALCA* **91**, 39-46, 1995.
- 28. Alexander, K. T. W., Covington, A. D., and Stosic, R. G.; "The Production of Soft Leather. Part 2. Drying and Stress Softening," *JALCA* 88, 271-277, 1993.